

# Correlated metals and the LDA+U method

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The purpose of this work is to investigate existing recipes for LDA+U calculations from the point of view of (i) their “first-principles” justification, (ii) their practical usefulness, and (iii) their effect on magnetic properties. We concentrate on the relatively new area of applying LDA+U to moderately-correlated, metallic systems. Our analysis of the Stoner instability for two most commonly used LDA+U functionals shows that neither of them correctly describes the essential physics of the correlated metals such as FeAl: (i) reducing the band dispersion by dressing of the one-particle excitation, and (ii) spin fluctuations near the quantum critical point. We show that the paramagnetism of FeAl is due to the spin fluctuations and cannot be explained within the LDA+U. A new form of the LDA+U functional is proposed.

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One of the most influential, from practical point of view, developments in the Density Functional Theory (DFT) in the last two decades was the LDA+U method (see, *e.g.*, Ref. [1]). This method includes the orbital dependence of the self-energy operators, missing from the Kohn-Sham potential, in a relatively crude, pseudo-atomic way, neglecting the fine details of the spatial variations of the Coulomb potential. On the contrary, the standard Local Density Approximation, LDA accounts for the spatial variation of the Hartree potential exceedingly well, but neglects the orbital dependence of the Coulomb interaction.

There is one inherent ambiguity in the LDA+U method: In LDA, all electron-electron interactions have already been taken into account in a mean field way. The Hubbard Hamiltonian, which represents the underlying physics of the LDA+U method, also incorporates a large part of the total Coulomb energy of the system. Simple combination of the LDA and Hubbard Hamiltonian thus leads to a double counting (DC) of the Coulomb energy, so one needs to identify those parts of the DFT expression for the total energy that correspond to the interaction included in the Hubbard Hamiltonian and subtract them. However, since the DFT Hamiltonian is written in terms of the total density, and the Hubbard Hamiltonian in the orbital representation, it appears impossible to build a direct link between the two. Second, even if it were possible, that would be undesirable. Spatial variation of the Hartree potential (and, to a lesser extent, the exchange-correlation potential) is very important. It would be unreasonable to subtract that out just because it is already taken into account in a primitive way (roughly speaking,  $UN^2/2$ ). Rather, one wants to identify the mean-

field part of the Hubbard Hamiltonian, and subtract *that*, leaving only the *correction* to the LDA-type mean field solution.

This is not a uniquely defined procedure. Several recipes exist, and it has been appreciated lately [2] that the results of LDA+U calculations may depend crucially on the choice of the DC recipe. It should be noticed that while in case of strongly correlated systems the LDA+U ideology is at least practically established, there is a relatively new area of applying LDA+U to moderately-correlated, metallic systems [2, 3, 4], where the situation is very far from clear.

In this Letter we will discuss the effect of different DC prescription on the LDA+U results in correlated metals. Our goal is to find out which problems associated with this class of materials can, in principle, be solved within LDA+U, and which cannot. We will also present a systematic approach to the DC problem, of which the existing recipes are special cases.

We shall use for our analysis the spherically averaged form of the rotationally-invariant LDA+U [5], due to Dudarev *et al.* [6]:

$$\begin{aligned} \Delta H_{LDA+U}^0 &= \frac{\bar{U}}{2} \sum_{m\sigma \neq m'\sigma'} n_{m\sigma} n_{m'\sigma'} - \frac{\bar{J}}{2} \sum_{m \neq m', \sigma} n_{m\sigma} n_{m'\sigma} \\ &= \frac{1}{2} \bar{U} N^2 - \frac{1}{2} \bar{J} \sum_{\sigma} N_{\sigma}^2 - \frac{1}{2} (\bar{U} - \bar{J}) \sum_{\sigma} \text{Tr}(\rho^{\sigma} \cdot \rho^{\sigma}) \quad (1) \end{aligned}$$

$$\Delta V_{LDA+U}^0(m\sigma) = \bar{U} N - \bar{J} N_{\sigma} - (\bar{U} - \bar{J}) n_{m\sigma} \quad (2)$$

Here  $\bar{U}$  and  $\bar{J}$  are spherically averaged Hubbard repulsion and intraatomic exchange for electrons with the given angular momentum (usually,  $l = 2$  or  $3$ ),  $n_{m\sigma}$  is the occupation number of the  $m$ -th orbital,  $\sigma = \pm 1$  is the spin index, and the superscript 0 means that the double counting terms have not been subtracted yet. The orbital occupation matrix matrix  $\rho_{mm'}^{\sigma} = -\pi^{-1} \text{Im} \int_{-E_F}^{E_F} G_{mm'}(E) dE$ , where  $G_{mm'}$  the one-electron Green's function;  $N_{\sigma} =$

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$\text{Tr}(\rho^\sigma)$  and  $N = \sum_\sigma N_\sigma$ .

Now we need to subtract from Eq. (1) the DC term, starting with the Hartree part of the Hubbard energy  $E_{LDA+U}^{\text{Hartree}} = \bar{U}N^2/2$ . The second term in Eq. (1) is also an explicit functional of the spin density only, and is also likely to be better described by LDA, so one can subtract it as well. What part of the remaining last term of the Eq. (1) is also included in LDA? Czyżyk and Sawatzky [7] suggested applying the LDA directly to this term, by assuming the uniform occupancy,  $\rho_{mm'}^{\sigma, LDA} = \delta_{mm'} n_\sigma$ , and writing down the corresponding DC term as

$$E_{D.C.} = \frac{1}{2}(\bar{U} - \bar{J})(2l+1) \sum_\sigma n_\sigma^2, \quad (3)$$

where  $n_\sigma = N_\sigma/(2l+1)$ . Eq. (3) leads to the following corrections to the total electronic energy and the effective potential:

$$\Delta E_{LDA+U}^{AMF} = -\frac{\bar{U} - \bar{J}}{2} \sum_\sigma (\text{Tr}(\rho^\sigma \cdot \rho^\sigma) - (2l+1)n_\sigma^2) \quad (4)$$

$$\Delta V_{LDA+U}^{AMF}(mm'\sigma) = -(\bar{U} - \bar{J})(\rho_{mm'}^\sigma - n_\sigma). \quad (5)$$

Here *AMF* stands for “Around Mean Field” [7].

For strongly correlated systems the limit of the uniform occupancy is not correct (in fact, it is not correct even in weakly correlated system due to the crystal field; it is easy to show that AMF therefore leads to an artificial enhancement of the crystal field splitting). Thus, it not surprising that for strongly localized electrons the AMF functional behaves pathologically. Consider, for example, Gd metal, with 7 occupied spin-up and 7 empty spin-down orbitals. The potential (5) has zero effect, as in this case  $n_{m\sigma} = n_\sigma$ . In reality, of course, the spin-up and spin-down bands form the lower and the upper Hubbard bands, respectively, and should be separated by a gap of the order of  $U$ . This observation led [7, 8] to another functional,

$$\Delta E_{LDA+U}^{FLL} = -\frac{\bar{U} - \bar{J}}{2} \sum_\sigma (\text{Tr}(\rho^\sigma \cdot \rho^\sigma) - (2l+1)n_\sigma) \quad (6)$$

$$\Delta V_{LDA+U}^{FLL}(mm'\sigma) = -(\bar{U} - \bar{J}) \left( \rho_{mm'}^\sigma - \frac{1}{2} \right), \quad (7)$$

which produces the correct limiting behavior in the strongly localized, limit, where  $\rho^\sigma \cdot \rho^\sigma = \rho^\sigma$ , and FLL stands for “Fully Localized Limit”. This functional can be obtained from the Eq. (1) by subtracting the following DC term:

$$\frac{1}{2}\bar{U}N(N-1) - \frac{1}{2}\bar{J} \sum_\sigma N_\sigma(N_\sigma-1), \quad (8)$$

which is the Hartree energy without the self-interaction, and the Stoner energy without the self-exchange. Most of the modern LDA+U calculations utilize one of these two functionals, although the real materials the occupation numbers lie between these two limiting cases.

Before analyzing further the behavior of the LDA+U functionals, let us briefly discuss what kind of corrections, qualitatively, we expect in a weakly-correlated metal (as opposed to an uncorrelated metal, on one hand, and a strongly-correlated insulator, on the other hand). We start from the Dyson’s equation,

$$\int d\mathbf{r}' [\hat{H}_0 + \Sigma(\mathbf{r}, \mathbf{r}', \varepsilon_{\mathbf{k}\alpha})] \psi_{\mathbf{k}\alpha}(\mathbf{r}') = \varepsilon_{\mathbf{k}\alpha} \psi_{\mathbf{k}\alpha}(\mathbf{r}), \quad (9)$$

where  $\varepsilon_{\mathbf{k}\alpha}$  and  $\psi_{\mathbf{k}\alpha}$  are the energies and the amplitudes of the poles of the one-particle Green’s function. The Kohn-Sham DFT approximates the self-energy operator  $\Sigma$  by the local, energy-independent potential,  $\Sigma(\mathbf{r}, \mathbf{r}', \omega) \approx V_{KS}(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')$ . In the lowest order in the screened interaction (the “GW” approximation), the correction to this appears to be a combination of two terms coming from the pole in the Green’s function (“dynamically screened exchange”) and the pole in the frequency-dependent interaction (“Coulomb hole”). The principal physics of this correction are thus the nonlocal and the dynamic (“fluctuational”) effects.

The LDA+U approach also corrects the Kohn-Sham equations, but in a different way: in addition to the local potential  $V_{KS}(\mathbf{r})$  a non-local operator is introduced which projects the state  $\psi_{\mathbf{k}\alpha}$  onto a set of  $m\sigma$  local orbitals. The goal is to remove or reduce orbital degeneracy at the Fermi level, in spirit of the unrestricted Hartree-Fock theory [9], rather than to account for fluctuations. The physics that is missing from the LDA+U and LDA equations can be described as exchange of virtual electronic excitations (cf. Fig. 1), roughly speaking, plasmons or (para)magnons. This leads to “dressing” of the one-particle excitations in the same way as the electron-phonon coupling “dresses” electrons near the Fermi surface, although in a correlated metal such mass renormalization effects occur on a large energy scale (of the order of  $U$  or  $J$ ). LDA calculations cannot reproduce such a dressing, which has been observed in many different ways experimentally. To give examples, LDA calculations do not explain large mass renormalizations in  $\text{Sr}_2\text{RuO}_4$  [10], and large specific heat renormalization in many correlated metals, produce too large plasma frequencies, *e.g.*, in  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , yield an optical absorption spectrum in  $\text{CrO}_2$  shifted by about 20% to higher frequency, as compared with experiment [11], and overestimate the exchange splitting in Ni by a factor of 2 [12]. In all these cases the total width of the *d*-bands is *decreased*, as opposed to *broadening* inherent to LDA+U. Here the essential physics is missing from the LDA+U as well as in LDA, while the spatial variation of the mean-field Coulomb interaction is treated better by the LDA. The missing physics is associated, to a large degree, with dynamic fluctuations. Indeed, the dynamic version of the LDA+U method, the Dynamic Mean Field Theory (DMFT) [13] resolves many of these problems.

For instance, the de Haas-van Alphen mass renormalization in  $\text{Sr}_2\text{RuO}_4$  is 3-4 [10], far greater than possible renormalization due to the phonons. Eliashberg-type cal-

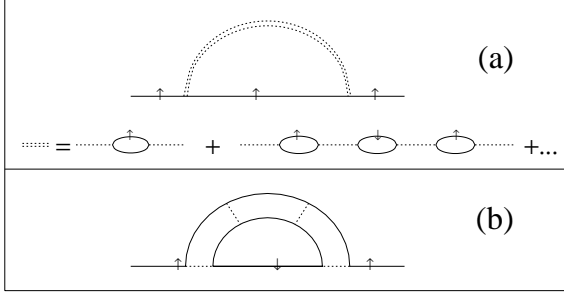


FIG. 1: Examples of the self-energy diagrams including exchange of virtual longitudinal (a) and transverse (b) paramagnons.

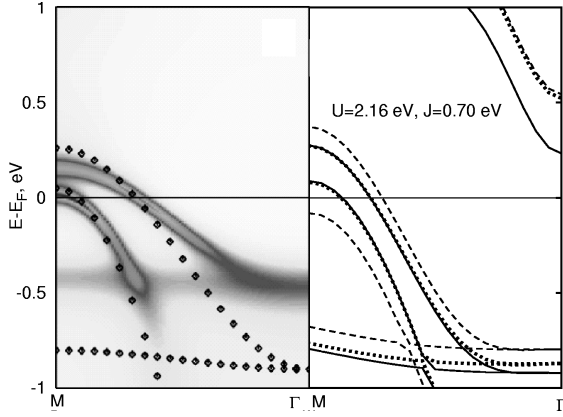


FIG. 2: Band structure of  $\text{Sr}_2\text{RuO}_4$  in LDA (dots in the left panel, solid line in the right panel) and in two flavors of LDA+U (right), and in the DMFT (left) [15].

culations [14] of the renormalization due to spin fluctuations, using a spectrum deduced from the LDA band structure, give mass renormalizations of the right order. Alternatively, when DMFT was applied to  $\text{Sr}_2\text{RuO}_4$ , it was shown that the dynamic effects near the Fermi level narrow the bands and increase their mass, in agreement with the experiment [15]. On the other hand, neither flavor of LDA+U has any interesting effect on these states (Fig. 2).

Another common problem is due to a quantum critical point, that is, to a magnetic instability at zero temperature. Fluctuations become increasingly important near such a point, effectively reducing tendency to magnetism. Examples include FeAl ( $M_{\text{LDA}} \approx 0.6 \mu_B$ ,  $M_{\text{exp}} = 0$ ),  $\text{Sr}_3\text{Ru}_2\text{O}_7$  ( $M_{\text{LDA}} \approx 0.8 \mu_B$ ,  $M_{\text{exp}} = 0$ ),  $\text{ZrZn}_2$  ( $M_{\text{LDA}} \approx 0.7 \mu_B$ ,  $M_{\text{exp}} = 0.2 \mu_B$ ), and other. LDA+U broadens the bands, and thus potentially reduces the tendency to magnetism. However, even when this happens, it happens for the wrong reason.

A metal becomes unstable against a ferromagnetic transition if its density of states at the Fermi level,  $D_F$  is larger than the so-called inverse Stoner parameter,  $1/I$ , where  $I$  is defined as  $I = \partial^2 E_{xc} / \partial M^2$ , the second derivative of the exchange-correlation energy with respect to the

total magnetic moment. In this language, the spin fluctuations near the quantum critical point effectively reduce  $I$ . This reduction overcomes some increase in the density of states.

In the LDA+U, the Stoner factor,  $D_F I$ , changes, not only because bands broaden and  $D_F$  decreases, but also because the newly added interaction energy depends on  $M$ . To get a better insight, let us use Eqs. (5, 7) when a metallic system is at the onset of the ferromagnetic phase transition. The force theorem, applied to the functionals in Eqs. (5) and (7), calls for a change in  $\rho_{mm'}^\sigma$ , namely  $\delta \rho_{mm'}^\sigma = b \sigma D_{mm'}$ , assuming a rigid shift of the bands by  $\pm b = \pm M / 2D_F$ , and a density of states (DOS) matrix  $D_{mm'} = -\pi^{-1} \text{Im } G_{mm'}(E_F)$ . This generates a change in the interaction energy, which results in an additional contribution to the Stoner parameter,

$$\begin{aligned} \Delta I_{AMF} &= (U - J) (\text{Tr}(D \cdot D) - (\text{Tr} D)^2 / (2l + 1)) / D_F^2 \\ \Delta I_{FLL} &= (U - J) \text{Tr}(D \cdot D) / D_F^2. \end{aligned} \quad (10)$$

In the limit of the uniform occupancy the latter expression reduces to  $(U - J) / (2l + 1)$ . Given that the LDA Stoner parameter,  $I$ , is of the same order as  $J$ , we obtain for the total Stoner parameter  $I_{FLL} \approx (U + 2lJ) / (2l + 1)$ , which the well known expression for the Stoner factor in the Hubbard model. On the contrary,  $\Delta I_{AMF}$  in this limit is zero. In real metals  $D_{mm'}$  is more complicated due to crystal field effects. Let us consider, for illustration, d-electrons in a cubic environment, and introduce the difference  $\Delta D = D_{eg} - D_{t2g}$ , where  $D_{eg}$  and  $D_{t2g}$  are  $e_g$  and  $t_{2g}$  DOS per one orbital at  $E_F$ , as a measure of the crystal field. This gives rise to a contribution to  $\Delta I_{AMF} = \frac{5}{24} (U - J) (\Delta D / D_F)^2$ . In some cases this contribution is not large enough to overcome a decrease in  $D_F$ , so that LDA+U may stabilize the paramagnetic state, as, for instance, observed for a very narrow range of unrealistically large  $U$ 's for FeAl by Mohn *et al.* [2] (of course, only in the AMF functional; the FLL functional produces a large  $\Delta I \approx (U - J) / 5$ , always increasing the tendency to magnetism). In reality, the ferromagnetic instability near a quantum critical point is suppressed by the fluctuations, and not due to an artificial enhancement of the crystal field (cf., also, Ref. [16]). Indeed, using DMFT, (which accounts for dynamic spin fluctuations [17]) with a realistic  $U = 2$  eV, we found the paramagnetic state to be perfectly stable, while the density of states was not reduced at all (Fig. 3).

These examples can be contrasted, say, with the d-bands in Cu metal. Despite the fact that Cu is a good metal, the d-bands in Cu are well localized and LDA+U is appropriate. Indeed, the LDA d-bands are 0.5 eV too high in Cu, while the FLL LDA+U d-bands are in excellent agreement with the experiment (Fig. 4).

We conclude that neither of the two available LDA+U functionals correctly describes the essential physics of the correlated metals: (i) reducing the band dispersion by dressing of the one-particle excitation, and (ii) spin fluctuations near the quantum critical point. One func-

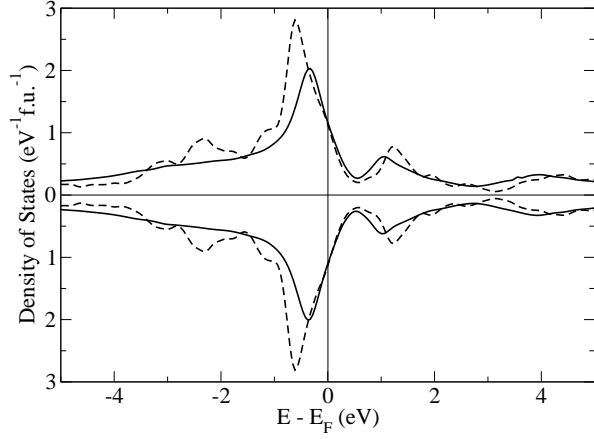


FIG. 3: FeAl density of states,  $D(E)$ , in DMFT (solid line) compared with the nonmagnetic LDA. The DMFT solution is stable, the LDA is not (a ferromagnetic solution is stable), despite the same  $D(E_F)$ .

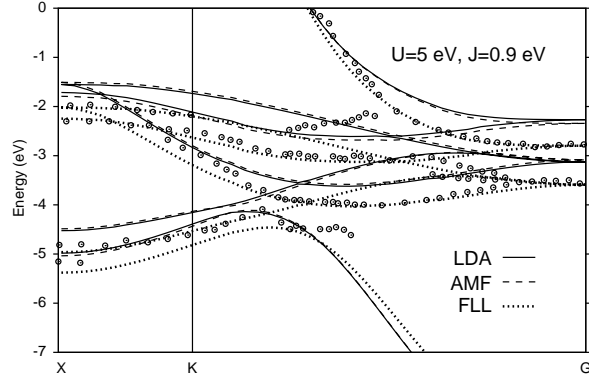


FIG. 4: Cu band structure in LDA and in two flavors of LDA+U. The experiment is from Ref. [18]

tional, labeled FLL here, correctly describes the important physics in the limit of well localized electrons (usually in insulators, but cf. the example of the Cu metal above), and can be recommended in this case. The other functional, labeled AMF, is exact in a hypothetical material with the uniform electron occupancies. Neither functional accounts for the fluctuation effects, but even in the static limit, the question arises, which functional is better in an intermediate, not-fully-localized limit? Below we suggest a recipe that accounts for an incomplete lo-

calization and reduces to AMF or FLL in the appropriate limits.

To determine the appropriate DC term, we need a mean field approximation to the last term in Eq. (1),  $(\bar{U} - \bar{J})n_{m\sigma}$ . This can be written as  $(\bar{U} - \bar{J})x_\sigma$ , where  $x$  is some function of  $n_\sigma$ . The AMF corresponds to  $x_\sigma = n_\sigma$ , while in the FLL  $x_\sigma = 1/2$ . Note that in the AMF the LDA+U potential, Eq. (5), averaged over all occupied states, is zero. This is a possible way to define a mean field (cf. the Slater approximation to the Fock potential), but not the way used in the DFT. The latter is a mean field theory that produces correct total energy, not the correct average potential. Thus AMF and FLL represent the “DFT” mean field if all occupation numbers are all the same, or are all 0 or 1, respectively. It is easy to show that  $(2l+1)n_\sigma^2 \leq \text{Tr}(\rho^\sigma \cdot \rho^\sigma) \leq (2l+1)n_\sigma$ , so that AMF always gives a negative, and FLL a positive correction to the total energy, while the right (in the DFT sense) DC subtraction should give zero correction to the total energy. Thus the “DFT”  $x_\sigma = \alpha_\sigma n_\sigma + (1 - \alpha_\sigma)(1/2)$ , and

$$\begin{aligned} \Delta E_{LDA+U}^{DFT} &= -\frac{\bar{U} - \bar{J}}{2} \sum_{\sigma} [\text{Tr}(\rho^\sigma \cdot \rho^\sigma) \\ &\quad - (2l+1) [\alpha_\sigma n_\sigma^2 + (1 - \alpha_\sigma)n_\sigma]] \\ \Delta V_{LDA+U}^{DFT}(mm'\sigma) &= -(\bar{U} - \bar{J}) [\rho_{mm'}^\sigma - \alpha_\sigma n_\sigma - \frac{1 - \alpha_\sigma}{2}]. \end{aligned}$$

Here

$$0 \leq \alpha_\sigma = \frac{\text{Tr}(\delta\rho^\sigma \cdot \delta\rho^\sigma)}{(2l+1)n_\sigma(1 - n_\sigma)} \leq 1. \quad (11)$$

We emphasize that  $\alpha_\sigma$  is not an adjustable parameter, and not a formal functional of the charge density, but a system-dependent constant, defined by the *self-consistent* occupation matrix and  $\delta\rho_{mm'}^\sigma = \rho_{mm'}^\sigma - n_\sigma$ . In practical calculations it needs to be recomputed at each iteration, as the current value of  $\rho_{mm'}^\sigma$  changes. Note that the total energy is given by the regular LDA expression that only implicitly depends on  $\bar{U}$  and  $\bar{J}$  *via* the changing density distribution; it is variational with respect to the charge density at the fixed  $\alpha_\sigma$ , but *not* variational with respect to  $\alpha_\sigma$  themselves.

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